Solubility is a determining factor in the synthesis, mixing ability and end-use of polymers. A general model for describing solubility (Flory, 1953) is discussed here with an emphasis on what information is obtained from SANS measurements from polymer solutions. SANS data from specific polymer solutions are discussed in some detail.

1. POLYMER SOLUTIONS BASICS

Most non-polar polymers dissolve in organic solvents and some polar polymers dissolve in water. Concentration ranges vary from dilute to semi-dilute to concentrated solutions. The borderline between the dilute and the semi-dilute regimes is referred to as the overlap concentration (c*) which is estimated as $c^* \sim M_w /(4\pi/3)R_g^{\,3}$ (M_w is the molecular weight and R_g is the radius of gyration). The polymer concentration c is related to the volume fraction ϕ through the density d as $c = \phi d$.

2. CASE OF A SIMPLE POLYMER SOLUTION

As an example of a polymer solution, the case of poly(ethylene oxide) PEO in water is discussed (Hammouda et al, 2002; Hammouda-Ho, 2007). The PEO monomeric unit -(CH_2CH_2O)- is the simplest one for a water-soluble polymer . When dissolved in water, PEO is characterized by hydrophilic interactions (hydrogen bonding of water molecules to the oxygen atoms on the polymer) and hydrophobic interactions (the CH_2CH_2 groups repel water). PEO dissolves in water for a wide range of temperatures and concentrations. Its homologues, PMO (-CH_2O-) and PPO (-$CH(CH_3)CH_2O$-) do not dissolve in water an ambient temperature. This may be due to the fact that the oxygen-oxygen inter-distance on the PEO chain matches the oxygen-oxygen inter-distance in the structure of pure water.

A typical SANS spectrum from a 4 % PEO/d-water (weight average and number average molecular weights of M_w = 100,000 and M_n = 96,000 g/mol respectively) is plotted for the T = 10° C temperature. This sample is well in the semi-dilute region (c* is estimated to be 0.0275 g/cm^3 which corresponds to 2.4 % volume fraction). The low-Q feature characterizes large size clusters (of no interest to us here) and the high-Q feature characterizes the polymer chains.

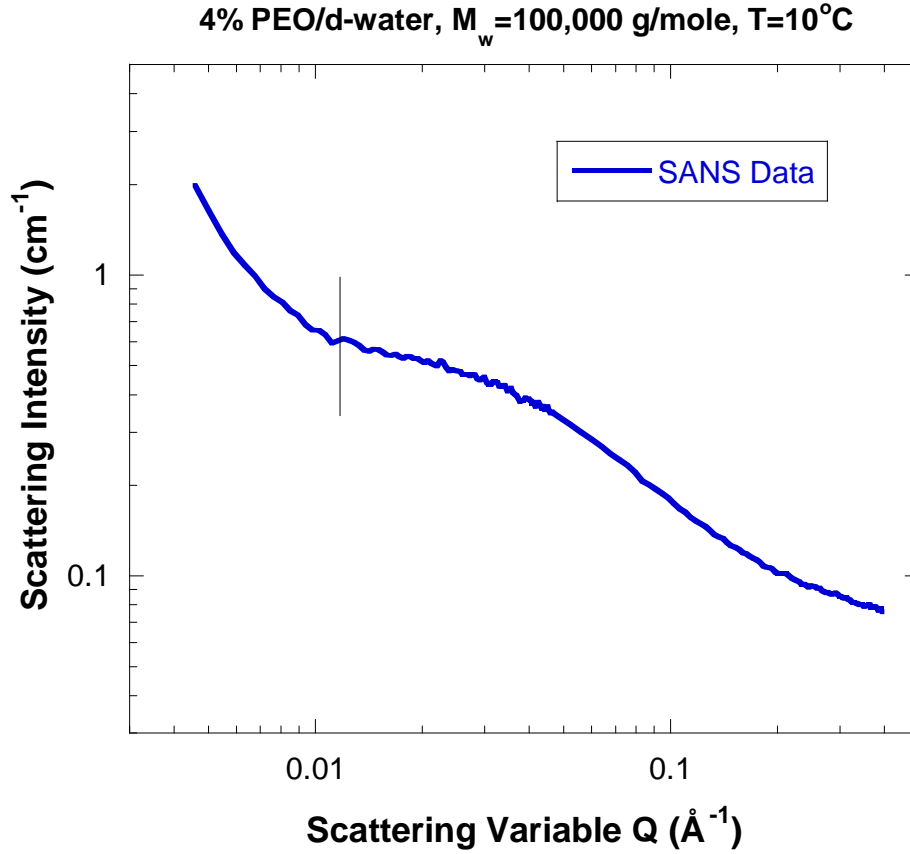**4% PEO/d-water, M$_w$=100,000 g/mole, T=10°C**

Figure 1: SANS data for a PEO/d-water sample over a wide Q range showing a low-Q feature and a high-Q feature. Only the tail of the low-Q feature is observed. Focus here is on the high-Q feature.

3. FIT TO A SIMPLE MODEL

In order to characterize our results, the following empirical functional form is fitted to the data:

$$I(Q) = \frac{A}{Q^n} + \frac{C}{1 + (Q\xi)^m} + B. \qquad (1)$$

The first term describes Porod scattering from clusters and the second term describes scattering from polymer chains. This second term characterizes the polymer/solvent interactions and therefore the thermodynamics and is of interest here. The two multiplicative factors A and C, the incoherent background B and the two exponents n and m are used as fitting parameters. The final parameter ξ is a correlation length for the entangled polymer chains. It gives an estimate of the entanglement length (average distance between entanglements). Non-linear least squares fits to the empirical functional form yield $\xi = 20$ Å, and $m = 1.9$ for the 4 % PEO/d-water sample. This empirical model

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should be used with caution since it does not reproduce the Guinier limit properly (except for m = 2).

4. <mark>THE CORRELATION LENGTH</mark>

The correlation length ξ decreases with increasing polymer volume fraction because the entanglement length increases. ξ goes from close to 80 Å at low polymer volume fraction to under 10 Å at high volume fraction. At low polymer volume fraction and at high-Q, the chains <mark>radius of gyration</mark> is given by $R_g = \sqrt{2}\,\xi = 113$ Å and the end-to-end chain distance is $R_{1n} = \sqrt{6}\,R_g = 277$ Å.
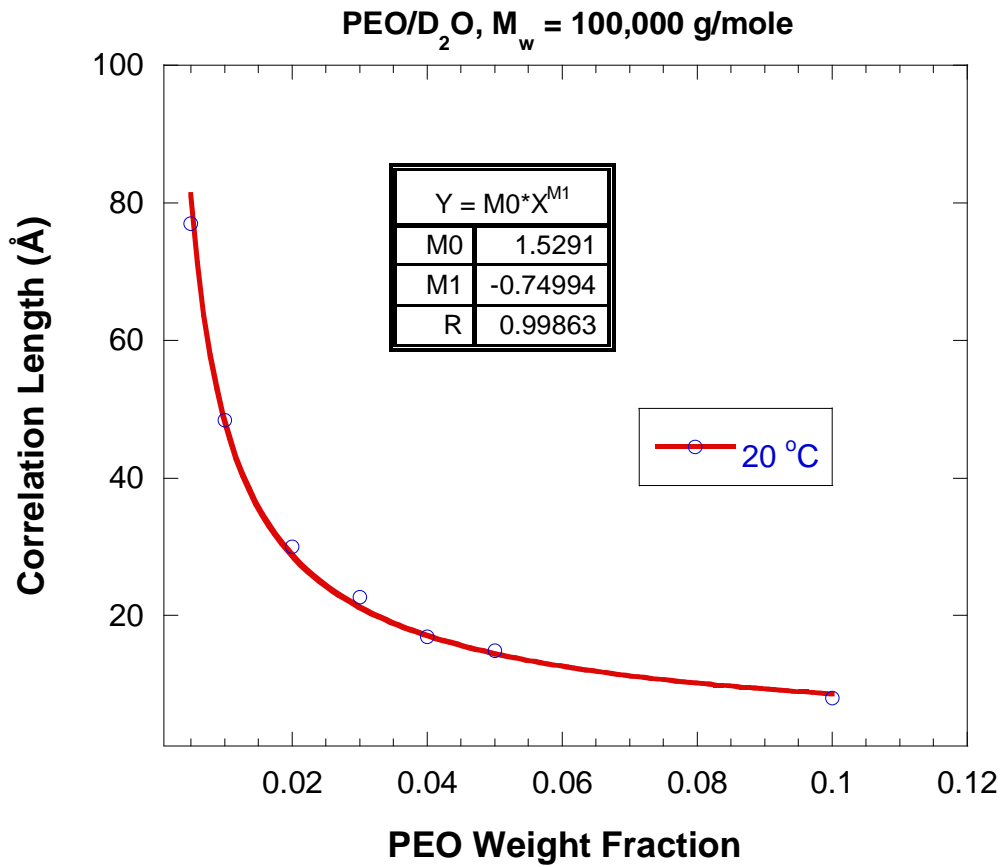

Figure 2: Variation of the <mark>correlation length</mark> with polymer volume fraction.

5. <mark>THE SPINODAL TEMPERATURE</mark>

The correlation length ξ and the <mark>coefficient C increase with increasing temperature T</mark> due to increased composition fluctuations <mark>when approaching phase separation</mark>. The <mark>PEO/d-water system is</mark> characterized by a lower critical solution temperature (<mark>LCST</mark>), i.e., it phase separates upon heating. The spinodal (phase separation) temperature T_s is obtained

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when C diverges; it can be accurately estimated from the intercept of a C^{-1} *vs* T^{-1} plot of data taken at various temperatures. In this case of 1 % PEO/d-water, one finds $T_s = 127$ $^{\circ}$C.
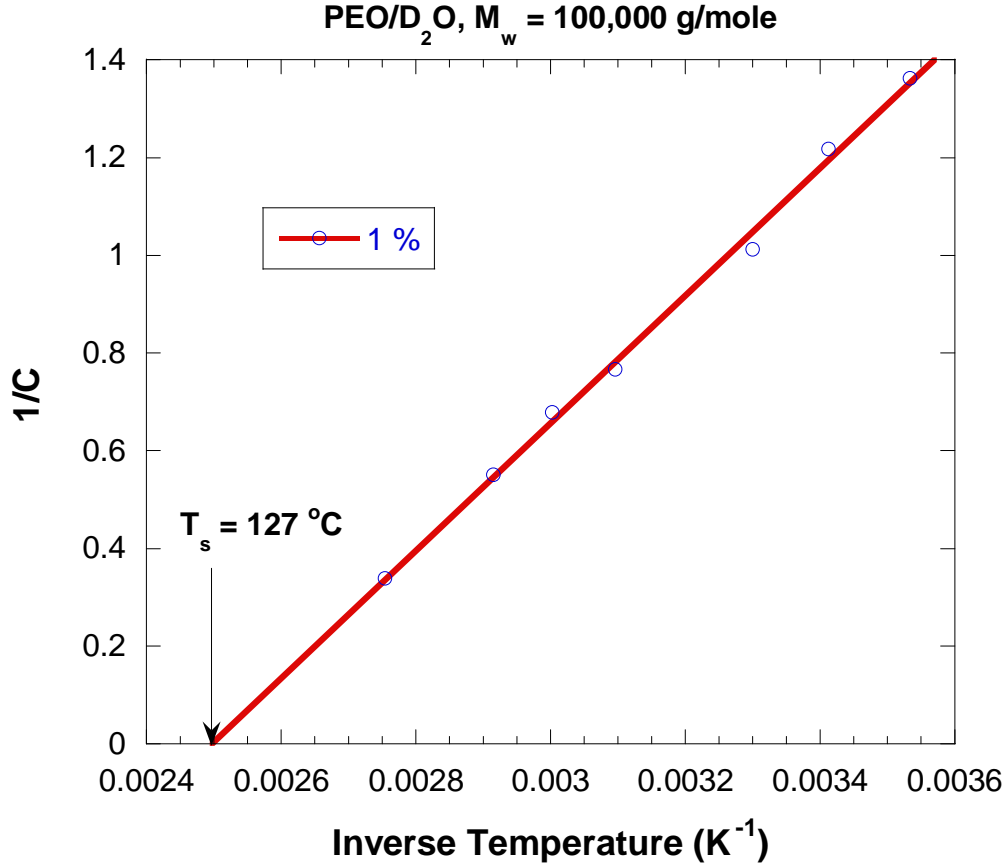
PEO/D$_2$O, M$_w$ = 100,000 g/mole

Figure 3: Variation of the high-Q inverse intensity C^{-1} with inverse temperature T^{-1}. The intercept represents the spinodal (phase separation) boundary line.

6. THE EXCLUDED VOLUME PARAMETER

Our fitting results (high-Q Porod exponent) for the 1 % PEO/d-water solution show that chains are mostly swollen at low temperatures (m = 1.85 which corresponds to an excluded volume parameter around $\nu = 1/m = 0.54$) and change to theta conditions at high temperatures (m = 2.02 which corresponds to an excluded volume parameter around $\nu = 0.5$) as the spinodal temperature is approached.
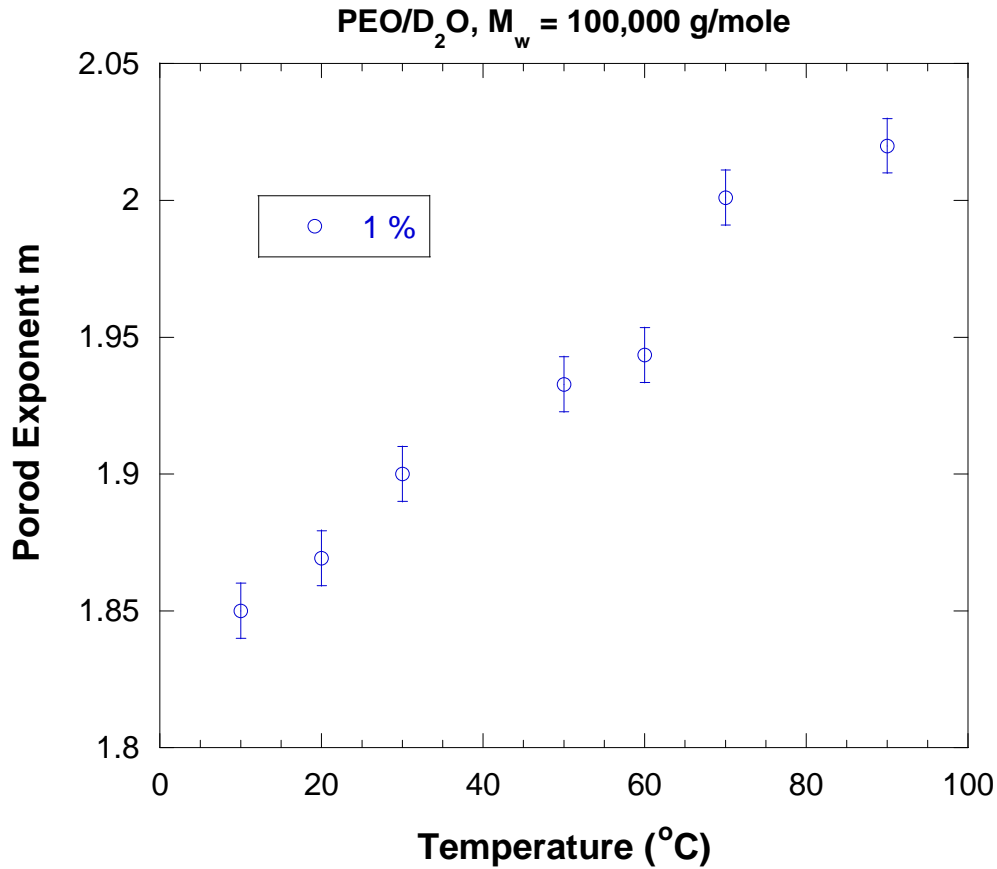
PEO/D$_2$O, M$_w$ = 100,000 g/mole

Figure 4: Variation of the Porod exponent with temperature. Polymer chains change from a swollen state to a "theta" condition as the spinodal temperature is approached.

7. BRANCH OF THE PHASE DIAGRAM

The spinodal temperature T_s was obtained from the various PEO volume fraction samples that were measured. A branch of the LCST phase diagram was obtained. What is interesting is that the phase boundary line T_s is estimated through extrapolation (i.e., before reaching it). For some of our samples, T_s happens to be above the boiling temperature of water (and therefore unreachable except when measurements are made inside a pressure cell). The SANS technique is a good monitor of phase separation because it is sensitive to composition fluctuations which get enhanced close to phase boundary lines.

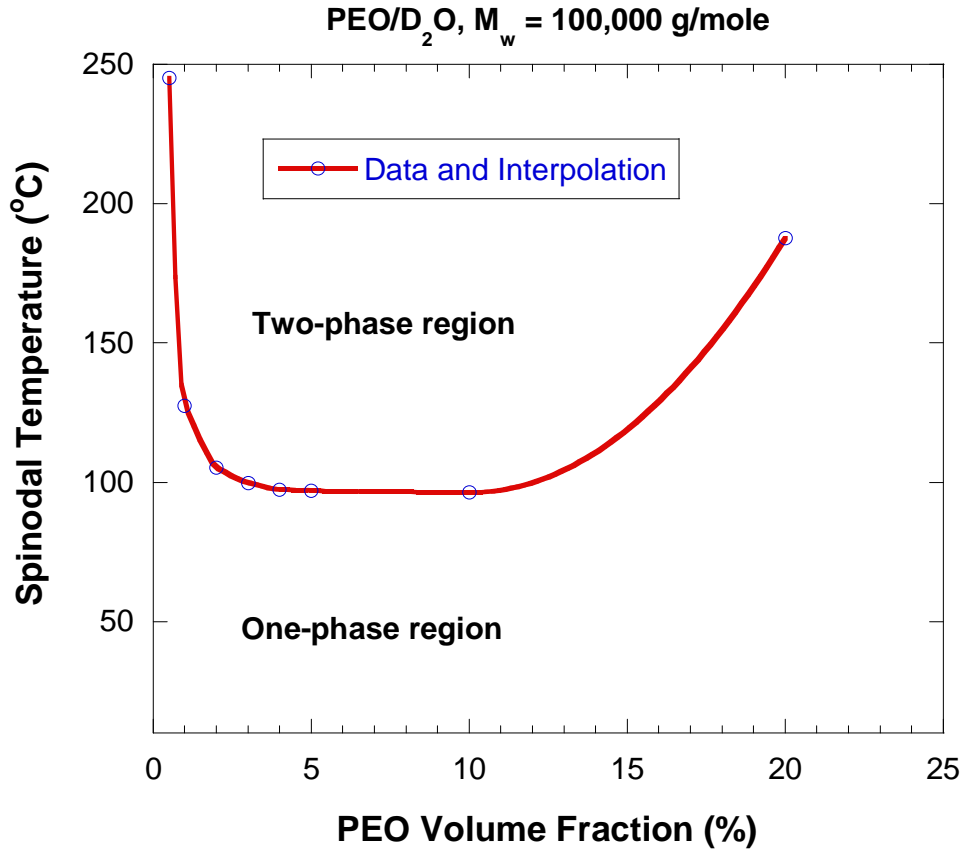**PEO/D$_2$O, M$_w$ = 100,000 g/mole**

Figure 5: Limited branch of the phase diagram for the PEO/d-water polymer solution system. Phase separation is obtained upon heating (LCST behavior).

8. POLYMER SOLUTION THERMODYNAMICS

Polymer solutions can phase separate upon heating (LCST behavior) or upon cooling (UCST behavior). Polymers that dissolve in organic solvents tend to be characterized by a UCST whereas water-soluble polymers tend to follow LCST thermodynamics. The Flory-Huggins approach is a mean-field theoretical model that predicts phase separation behavior. This model will be discussed later for polymer blends.

9. THE ZERO AVERAGE CONTRAST METHOD

The zero average contrast method (also called "high concentration" method) uses variation of the fraction of deuterated polymer and deuterated solvent but keeping the total polymer concentration (or volume fraction) constant to measure the single-chain form factor even at high concentrations because the interchain contribution cancels out.

A series of PEO/water solutions were prepared whereby the total polymer fraction was kept constant (volume fraction of 4 %) but the relative amount of dPEO/hPEO was

varied. In order to isolate the single-chain contribution, we used mixtures of D_2O and H_2O solvent molecules that match the average polymer scattering-length density in each case. For such hPEO/dPEO/H_2O/D_2O mixtures, the scattering intensity is given by:

$$\frac{d\Sigma(Q)}{d\Omega} = \left(\left\{ \Delta B_P{}^2 \right\} - \left\{ \Delta B_P \right\}^2 \right) n_P \phi_P v_P P_S(Q) + \left\{ \Delta B_P \right\}^2 n_P \phi_P v_P P_T(Q) \quad (2)$$

$$\left\{ \Delta B_P{}^2 \right\} = \left[\Delta \rho_D{}^2 \frac{\phi_D}{\phi_P} + \Delta \rho_H{}^2 \frac{\phi_H}{\phi_P} \right]$$

$$\left\{ \Delta B_P \right\}^2 = \left[\Delta \rho_D \frac{\phi_D}{\phi_P} + \Delta \rho_H \frac{\phi_H}{\phi_P} \right]^2$$

$$\Delta \rho_D = \left(\rho_D - \rho_S \right) = \left(\frac{b_D}{v_D} - \frac{b_S}{v_S} \right)$$

$$\Delta \rho_H = \left(\rho_H - \rho_S \right) = \left(\frac{b_H}{v_H} - \frac{b_S}{v_S} \right).$$

Here, b_H and b_D are the scattering lengths for the hPEO and dPEO monomers, v_H and v_D are the corresponding specific volumes, and ϕ_H and ϕ_D are the corresponding polymer volume fractions (and similarly for the solvent scattering length density b_S/v_S). In order to arrive at this formula, it was assumed that the protonated and deuterated polymer degrees of polymerization and specific volumes are matched. The degree of polymerization used here, n_P, represents the value for the two mixed polymer species ($n_H = n_D = n_P$). The total polymer volume fraction ϕ_P ($\phi_P = \phi_H + \phi_D$) and polymer specific volume v_P ($v_P = v_H = v_D$) have also been defined. The single-chain form factor $P_S(Q)$ and the total-chain structure factor (including intra-chain and inter-chain contributions) $P_T(Q)$ have also been defined. The average contrast match condition zeroes the second term in the cross section equation leaving only the first term proportional to $P_S(Q)$.

This formula assumes that deuteration does not affect chain structure or interactions. This is obviously an assumption for our hydrogen-bonded system.
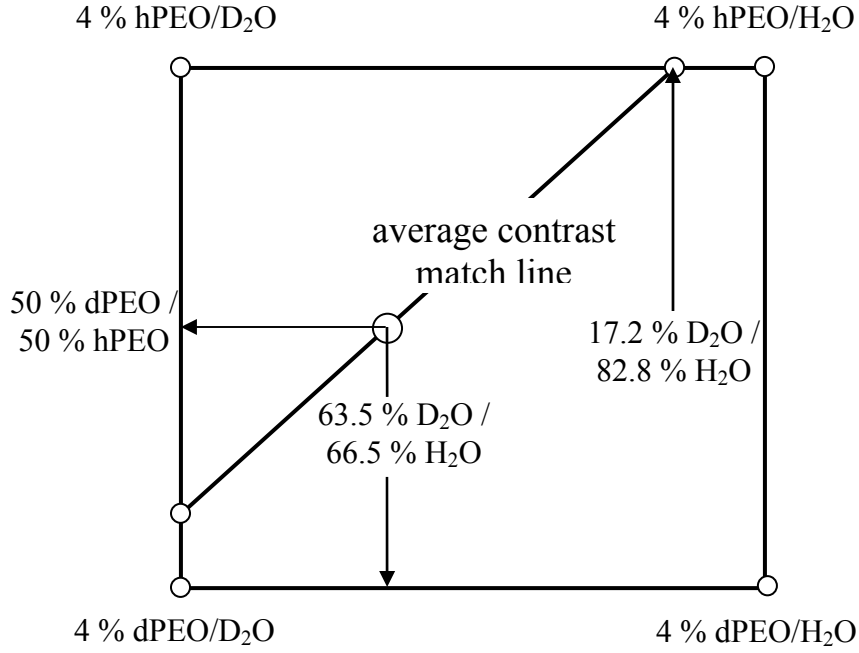
Figure 6: The series of PEO/water solutions for the average contrast match series. Mixtures of deuterated and non-deuterated polymers (dPEO and hPEO) and solvents (D_2O and H_2O) are used.

Specific values for the defined parameters for our system are as follows.

$$n_{hPEO} = 2273, \; n_{dPEO} = 2125, \qquad\qquad (3)$$
$$b_{hPEO} = 4.14*10^{-13} \text{ cm}, \; b_{dPEO} = 45.78*10^{-13} \text{ cm},$$
$$b_{H_2O} = -1.67*10^{-13} \text{ cm}, \; b_{D_2O} = 19.14*10^{-13} \text{ cm},$$
$$v_{hPEO} = v_{dPEO} = 38.94 \text{ cm}^3/\text{mol},$$
$$v_{H_2O} = v_{D_2O} = 18 \text{ cm}^3/\text{mol}.$$

The four possible contrast factors corresponding to the 4 corners in the figure are as follows:

$$\left(\frac{b_{dPEO}}{V_{dPEO}} - \frac{b_{H2O}}{V_{H2O}} \right)^2 N_{av} = 9.66*10^{-3} \text{ mol}/\text{cm}^4 \qquad\qquad (4)$$

$$\left(\frac{b_{hPEO}}{V_{hPEO}} - \frac{b_{D2O}}{V_{D2O}} \right)^2 N_{av} = 5.50*10^{-3} \text{ mol}/\text{cm}^4$$

$$\left(\frac{b_{hPEO}}{V_{hPEO}} - \frac{b_{H2O}}{V_{H2O}} \right)^2 N_{av} = 2.38*10^{-4} \text{ mol}/\text{cm}^4$$

$$\left(\frac{b_{dPEO}}{V_{dPEO}} - \frac{b_{D2O}}{V_{D2O}} \right)^2 N_{av} = 7.53*10^{-5} \text{ mol}/\text{cm}^4 .$$

Here, we have multiplied by Avogadro's number ($N_{av} = 6.022*10^{23}$ molecules/mol) for convenience. The strongest neutron contrasts correspond to the two mixtures: dPEO/H_2O and hPEO/D_2O. Contrasts corresponding to the other two mixtures are much lower. The higher incoherent background is found in the samples with the most hydrogen (i.e., with non-deuterated solvent).

Data from a specific 4 % PEO/water mixture with 50 % dPEO/50 % hPEO and 63.5 % D_2O / 36.5 % H_2O are shown in a figure. This mixture is represented by a circle on the average contrast match line in the same figure. This sample is characterized by the single-chain scattering feature only. The low-Q feature representing clustering has mostly disappeared. This method is useful for isolating single-chain properties in semi-dilute (and even concentrated) polymer solutions.
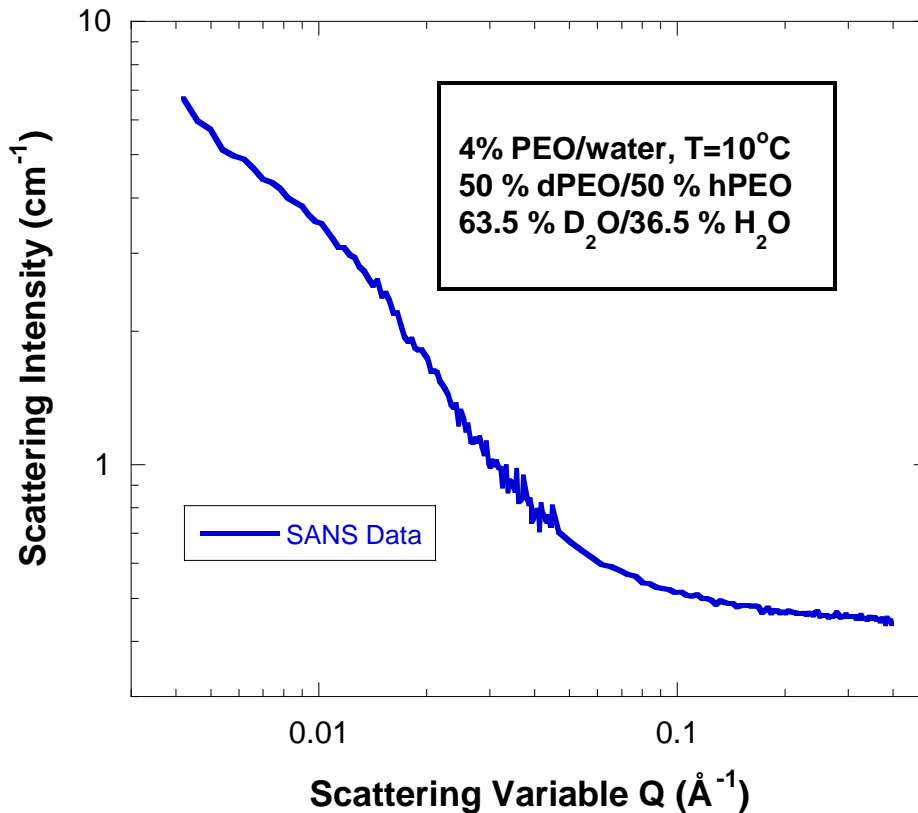

Figure 7: SANS data from a PEO/water sample on the average contrast match line. Mixtures of dPEO/hPEO and D_2O/H_2O are used to cancel out scattering from the clusters leaving scattering from single polymer chains only. M_w = 100,000 g/mol for both the dPEO (deuterated) and hPEO (non-deuterated) polymers.

Nonlinear least-squares fit of this data to the Gaussian chain model with excluded volume (described before) gave a segment length of a_{PEO} = 6.7 Å and an excluded volume parameter of v = 0.51. Based on these numbers, the radius of gyration can be estimated as

$$R_g = \frac{a_{PEO} \, n_{PEO}^{0.51}}{\sqrt{(2v+1)(2v+2)}} = 137 \text{ Å}.$$ The PEO chain degree of polymerization $n_{PEO} = 2200$ has been used.

Fit to the simple "empirical model" form (described before) gave a correlation length $\xi = 92.8$ Å and a Porod exponent $m = 2.06$. The radius of gyration can be estimated here also as $R_g = \sqrt{2}\,\xi = 131$ Å. This shows acceptable agreement.

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QUESTIONS

1. What is the high-Q expansion of the Debye function (form factor for Gaussian coil)?
2. What standard plot is used to obtain the radius of gyration, the correlation length, the persistence length?
3. What is the meaning of the correlation length?
4. What does it mean to refer to the PEO/water solution as characterized by an LCST phase diagram?
5. A Porod exponent of 5/3 is an indication of what type of polymer chains?
6. The high-Q SANS data is characteristic of what type of interactions in polymer solutions?

ANSWERS

1. The high-Q expansion of the Debye function is: $\text{Lim}\, P(Q \to \infty) = 2/(Q^2 R_g^{\,2})$.
2. The Guinier plot is used to obtain the radius of gyration, the Zimm plot is used to obtain the correlation length, and the Kratky-Porod plot is used to obtain the persistence length.
3. The correlation length is the average distance between entanglement points.
4. The PEO/water solution is characterized by a Lower Critical Solution Temperature phase diagram means that phase separation occurs upon heating.
5. A Porod exponent of 5/3 is an indication of fully swollen polymer chains.
6. The high-Q SANS data is characteristic of solvent/polymer interactions (the so-called solvation shell) and therefore of the thermodynamics of mixing.